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CHAPTER XXI

HIGH-AMYLOSE CORN STARCH: ITS PRODUCTION, PROPERTIES, AND USES

By F. R. Senti

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I. Introduction

Except for the waxy starches that consist only of the branched component, amylopectin, nearly all starches also contain 20% to 30% of the linear component, amylose. No starches are known that contain amylose as the sole constituent, and only one plant source has been found which, without genetic improvement, produces starch that contains more than 50% of amylose. This is the wrinkled-seeded pea whose starch analyzes 60–70% amylose (*1–3*). No attention has been given this starch for possible industrial use because its total content in peas is low and separating it from the protein matrix of the seed is difficult.

Hybrid corn varieties are now available which produce starches that contain more than 50% "apparent"[2] amylose. Such high-amylose corn

[1] This is a laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture.

[2] Throughout this chapter the term "apparent" is used or understood in reference to the amylose content of high-amylose starches because the branched fraction in such starches, unlike that in ordinary starch, accounts for a substantial part of the iodine binding on which the analyses for amylose are based. Apparent amylose contents therefore are higher than true values; fractionation studies indicate that about 80% of the apparent amylose content can be isolated by 1-butanol precipitation.

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varieties that are agronomically adapted to commercial production are designated by the generic term "amylomaize" (4). In contrast to wrinkled-seeded peas, which have been grown as a garden vegetable for a long time, these new corn hybrids have been systematically developed by corn breeders with the aid of chemists to achieve a unique starch composition. Development of the new amylomaize hybrids stemmed from the discovery of a mutation in an inbred line of corn that doubled the amylose in ordinary corn from 27% to 55% without appreciable increase in water-soluble polysaccharides.

Amylose level varies not only with background dent lines containing different modifying factors but also within the population of individual

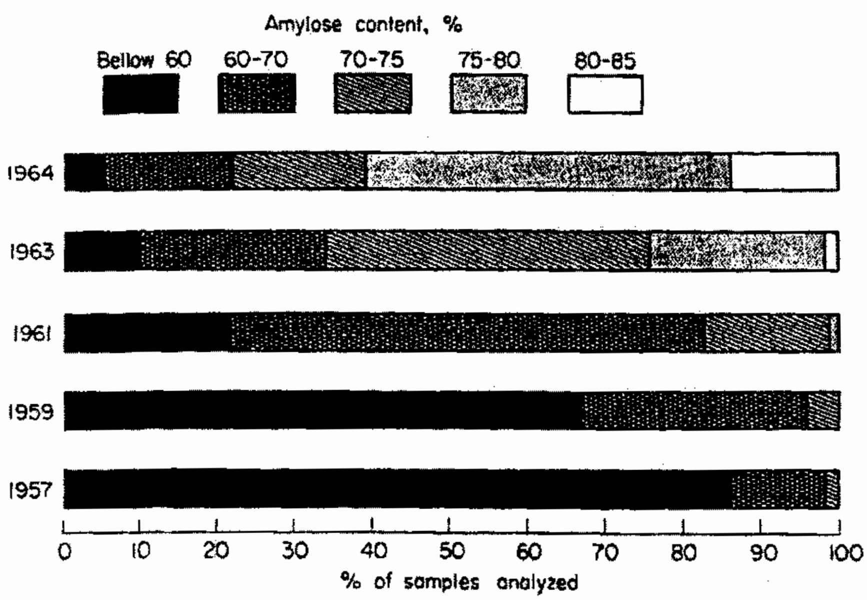

FIG. 1.—Progressive increase in apparent amylose content in samples of high-amylose corn lines.

inbred lines carrying the amylose-enhancing genes. The development of high-amylose hybrids involves thousands of amylose analyses each year in the selection and reselection for high amylose from the large population within gene source stocks, from backcrossed inbred lines, and from the lines bearing combinations of desired genes which are made up from the inbred lines. Good progress has been made toward the development of true-breeding progeny containing over 80% amylose, as illustrated in Figure 1. These analytical results obtained by the Northern Laboratory and cooperating breeders show a steady rise over the past 7 years in the percentage of samples analyzed that fall in the higher amylose ranges. Many samples now exceed the 80% apparent amylose level, and it

appears that substantial increases in amylose content will continue to be achieved in the next few years by application of present breeding methods.

The continuous range of amylose contents, resulting from the interaction of specific genes for amylose with the gene modifiers present in various background lines, makes possible the development of amylomaize hybrids containing from 50% upward of amylose. The first double-cross hybrids to be developed had 57% apparent amylose in their starch; these hybrids were grown in 1958 on a scale sufficient for experimental processing in a commercial wet-milling plant. Increasing quantities were grown and processed in subsequent years, and this starch, often designated as a Class 5 amylomaize starch because its amylose content lies in the 50% to 60% range, is now an established commercial product. As the agronomic properties of the Class 5 hybrid were improved, the amylose content of the starch also increased slightly until the 1963 crop was analyzed at 62.1% apparent amylose. Sufficient acreage of a Class 6 single-cross hybrid was grown in 1959 for experimental processing studies and investigation of starch properties in the 60% to 70% amylose range. Amylose content of the starch produced was 67%. The first sizable planting of Class 7 amylomaize (70–80% amylose) was made in 1963, and starch from this corn became available on a limited commercial basis. The amylose content of this starch was about 73%. A Class 8 amylomaize (80% plus amylose) is currently available for experimental purposes.

II. Kernel Properties of Amylomaize

In the development of amylomaize as a source of industrial starch, a major goal has been to increase the amylose level without undue sacrifice of starch yield. The first high-amylose endosperm genotypes that were studied were characterized by large decreases in starch as the amylose level was increased. Discovery of the *ae* gene provided the basis for the development of amylomaize varieties with starch contents near those of ordinary dent corn lines. In Table I the composition of grain from Classes 5, 6, 7, and 8 amylomaize hybrids is compared with that of ordinary dent corn *(5–9)*. Starch content of the amylomaize hybrids ranges from 57.9% to 66.4%, compared to 73.8% for the ordinary dent hybrid. Note that both Class 5 and Class 7 amylomaize increased in starch content after their first introduction reflecting selection for agronomic improvement and starch yield.

Protein content of amylomaize hybrids (Table I) is substantially higher than that of ordinary dent corn; some hybrids have over 14% of protein compared with 10% in ordinary dent corn listed in the table.

Table I

Composition[a] of Ordinary Dent Corn and Amylomaize[b] by Amylose Content and Crop Year

Constituent	Ordinary dent corn 1956 (%)	Amylomaize (class and year): Class 5 1958 (%)	Class 5 1960 (%)	Class 5 1963 (%)	Class 6 1959 (%)	Class 7 1960 (%)	Class 7 1963 (%)	Class 8 1964 (%)
Apparent amylose	24	57	57.8	62.1	66.7	74.6	73.3	80.0
Starch	73.8	62.7	60.6	63.5	66.4	58.1	61.1	57.9
Protein	10.1	13.9	12.5	12.0	11.3	14.5	11.9	13.7
Crude fat	4.5	7.1	6.6	7.1	5.2	7.3	7.0	5.9
Solubles	5.6	8.6	—	9.1	7.1	—	10.0	—
Total sugars	2.3	2.6	—	1.8	3.4	—	1.8	—

[a] Moisture-free basis.

[b] All amylomaize varieties were hybrids grown in commercial plantings except Class 6 and 1960 Class 7 which were experimental hybrids.

As in ordinary dent corn (*10*), the data of Table I suggest an inverse relationship between starch and protein content for amylomaize. Zuber and co-workers (*11*) found a highly significant negative correlation ($r = -0.80$) between endosperm protein and starch content for their high-amylose inbred lines. It may be expected, therefore, that, as starch is increased in amylomaize hybrids by genetic improvement, protein will approach the levels found in ordinary dent corn.

Fat content in the whole grain from amylomaize hybrids (Table I) ranges from 5.2% to 7.1% as compared to 4.5% in the ordinary dent hybrid listed in the table. Hubbard and co-workers (*12*) reported the same value for the average of all grades of dent corn received at principal markets in 1952–1954; it is evident that present amylomaize varieties contain substantially more oil and that a greater recovery of this by-product may be expected in commercial processing.

The relative proportions and composition of the endosperm, germ, and bran fractions in the amylomaize kernel (*13, 14*) provide a basis for estimating the possible yield of various kernel constituents in a wet-milling operation. Relative proportions of kernel fractions for Classes 5, 6, and 7 amylomaize hybrids are presented in Table II; starch, fat, protein, and ash content of these fractions are given in Table III for Class 5 and Class 6 hybrids. Composition of ordinary dent corn is given in each table for comparison. These amylomaize hybrids contain somewhat less endosperm, more germ, and considerably more bran than ordinary dent corn (Table II). The lower starch content of the amylomaize kernel (Table I) results not only from the lower proportion of endosperm but also from the presence of less starch in the endosperm than that of ordinary corn

Table II

Proportion of Kernel Fractions in Ordinary Dent Corn and Amylomaize of Different Amylose Contents

Fraction	Ordinary dent corn[a]	Amylomaize (class and year) Class 5 1958[b] (%)	Class 5 1963[c] (%)	Class 6 1959[b] (%)	Class 7 1963[c] (%)
Amylose content	27.0[d]	57.0	62.1	66.7	73.3
Endosperm	82.0	76.5	78.3	78.9	77.6
Germ	11.7	14.2	13.7	13.1	13.8
Bran	5.6	9.2	8.0	8.0	9.1

[a] Average of five different yellow dent hybrids (*10*).
[b] Data from reference *13*.
[c] Data from reference *14*.
[d] Data from reference *27*.

Table III

Composition of Kernel Fractions of Amylomaize[a] and Ordinary Dent Corn[b]

Constituent	Endosperm Ordinary dent (%)	Endosperm Class 5 1958 (%)	Endosperm Class 6 1959 (%)	Germ Ordinary dent (%)	Germ Class 5 1958 (%)	Germ Class 6 1959 (%)	Bran Ordinary dent (%)	Bran Class 5 1958 (%)	Bran Class 6 1959 (%)
Ash	0.36	0.42	0.42	10.33	8.98	9.08	0.73	1.11	1.31
Protein	7.8	12.2	10.4	18.5	17.2	19.0	3.5	6.2	7.3
Crude fat	0.8	1.7	0.93	33.9	36.1	28.9	1.0	3.92	4.36
Starch	87.3	80.0	82.3	8.1	9.52	12.5	7.3	4.02	4.03

[a] Data from reference *13*.
[b] Average of five different yellow dent hybrids (*10*).

(Table III). The relatively higher fat content of the endosperm and bran as compared to ordinary corn (Table III) indicates that the oil recovery from amylomaize cannot be expected to be as high as the total fat content of the kernel (Table I) would suggest. A greater yield of oil in a wet-milling operation is possible, however, because of the larger germ fraction in amylomaize.

III. Production of Starch by Wet Milling Amylomaize

The recovery of starch and oil to be expected from amylomaize in commercial processing can be judged from laboratory and small-scale

pilot-plant wet-milling experiments. Anderson and co-workers (*5–7*) have evaluated the wet-milling properties of amylomaize as the new hybrids have become available. Some of their results are presented in Table IV along with later data of Anderson (*8*) on the 1963 crops of

Table IV

Comparison of Processing Characteristics of Amylomaize and Ordinary Dent Corn

	Ordinary dent corn	Amylomaize						
		Class 5			Class 6	Class 7		Class 8
Characteristic	1956 (%)	1958 (%)	1960 (%)	1963 (%)	1959 (%)	1960 (%)	1963 (%)	1964 (%)
Kernel swelling	63	128	110	96	105	125	110	105
Steep water								
Solids	4.2	3.6	4.6	4.7	4.2	3.7	5.4	4.2
Protein	31.2	31.0	25.4	29.0	29.0	29.0	29.1	26.3
Starch								
Yield	64.4	43.5	43.8	46.6	50.8	42.0	43.8	41.0
Recovery	87.3	71.4	71.8	73.0	82.7	71.6	71.4	70.3
Protein	0.51	0.7	0.46	0.52	0.48	0.59	0.52	0.8
Squeegee starch								
Yield	—	4.9	2.9	2.7	4.1	2.5	4.5	—
Protein	—	5.0	9.4	5.0	9.2	4.5	3.7	—
Starch	—	94.4	81.8	92.5	81.9	85.7	—	—
Germ								
Yield	4.7	6.5	—	—	7.6	—	—	—
Oil	53.0	56.0	—	—	41.2	—	—	—
Gluten								
Yield	7.8	15.5	19.4	16.0	11.2	17.7	14.9	17.7
Protein	44.2	33.1	26.2	28.6	34.6	32.3	26.7	27.2
Starch	45.0	52.3	48.1	50.5	44.2	40.7	54.7	—

Class 5 and Class 7 amylomaize, and on the 1964 crop of Class 8 amylomaize (*9*).

An unexpected property of amylomaize is its greater swelling as measured by over-all volume occupied by the grain in the tank on steeping 48 hr. in 0.25% sulfur dioxide at 52°. Under these conditions ordinary corn (Table IV) swells 63% in volume, amylomaize, 96 to 128%. In swelling, amylomaize absorbs a correspondingly greater amount of water than does ordinary corn (*5, 6*). The greater imbibition of water by amylomaize kernels during steeping is consistent with the greater percentage of solubles (Table I) in the amylomaize samples (7.1–10.0%) as compared to ordinary dent corn (5.6%). The lack of

increased yield of solids in the steep water (Table IV) shows that the additional solubles in the amylomaize are not extracted during steeping of the whole grain but are retained inside the kernel where they can exert an osmotic effect.

Starch yield in percentage of grain weight (Table IV) is lower for the amylomaize samples than for ordinary dent corn. This difference would be expected from the lower starch content of the amylomaize. A better index of milling quality, however, is the percentage of starch recovered. Starch recovery in laboratory milling ranges from 70.3% to 82.7% for the amylomaize hybrids as compared to 87.3% for ordinary dent corn. Class 6 amylomaize is outstanding for its starch recovery, and compares favorably with ordinary dent corn in this respect. The generally lower starch recovery from amylomaize has been attributed to difficulties in separation of small and irregularly shaped granules present in these grains (*5–7*). In Table V the distribution of granule sizes shown

Table V

Average Granule Diameters of Amylomaize and Ordinary Dent Corn Starches

Diameter	*Ordinary dent corn* *US 13 hybrid* (*microns*)	*Amylomaize* *Class 5* *1963* (*microns*)	*Class 6* *1959* (*microns*)	*Class 7* *1962* (*microns*)
Number-average	10.6	6.6	8.9	7.5
Weight-average	15.5	10.9	12.7	11.4

for Class 6 amylomaize starch is closest to that of ordinary dent corn. The poorer separation of amylomaize starch from the protein matrix is evident from the higher starch and lower protein content of the amylomaize gluten fractions and their greater yield, as compared to ordinary dent corn. Further loss in prime starch yield occurs in the additional tabling operation required to reduce the protein content of the amylomaize starch to a level comparable to that in ordinary dent starch. The squeegee starch fraction recovered in this operation represents 2.1–4.6% of starch yield.

IV. Properties of Amylomaize Starch Granules

Granules of the amylomaize starches differ considerably from ordinary corn starch in morphology, birefringence, size, x-ray pattern, gelatinization, swelling, and solubility properties. A comparison of size and shape of Classes 5, 6, and 7 amylomaize starches with ordinary dent corn starch can be made from the photomicrographs in Figure 2. An

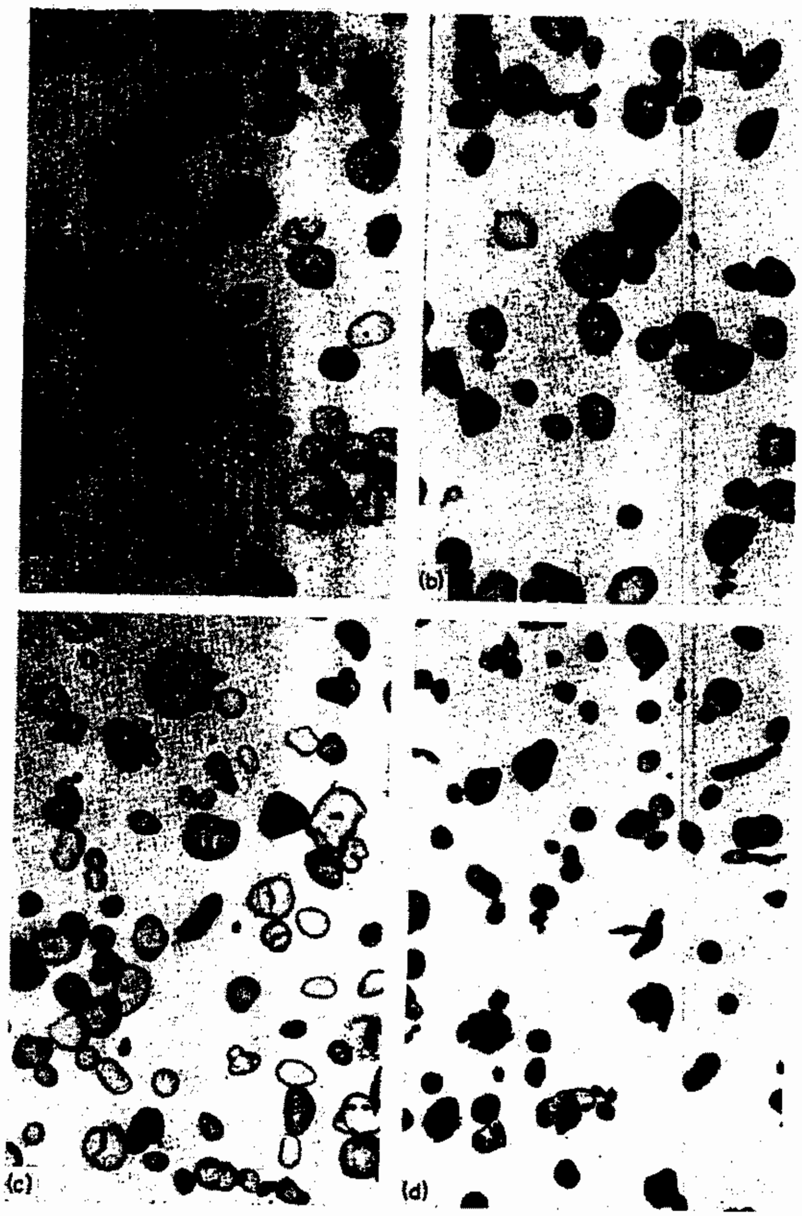

FIG. 2.—Photomicrographs of ordinary dent corn starch and three classes of amylomaize starches stained lightly with iodine: a, ordinary dent corn starch from a Holmes hybrid; b, amylomaize starch, Class 5, 61.8% amylose; c, amylomaize starch, Class 6, 66.7% amylose; d, amylomaize starch, Class 7, 72.1% amylose; 500 × magnification.

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obvious difference in the amylomaize starch granules is their smooth surface as compared to the faceted surface of ordinary corn starch. Another characteristic of the amylomaize starches is the presence of granules of unusual shape. Compound granules are fairly numerous and are generally in the size range of the other granules. The elongated or filamentous granules, which may be simple or branched, are most interesting. These are most evident in the photomicrograph of Class 7 starch (Fig. 2d). The elongated granules are frequently thin, but others are short and stubby with thickening at one end or along the filament. A small number of granules have been observed to be a knotted mass of outgrowths. An example of this type of granule appears in the upper center portion of Figure 2c. This type is the one referred to by Badenhuizen *(15)* as "grape" structures. Such granules were more numerous in some of the earlier Class 5 selections but apparently have been bred out of the latest crosses.

1. Granule Birefringence and Iodine Staining

A large proportion of the granules of amylomaize starches are approximately spherical in shape and differ from ordinary corn starch only by lack of a faceted surface. However, when examined between crossed Nicols, many of these granules do not show the polarization cross characteristic of starch *(16)*. This type of granule occurs most frequently in Class 7 starch. The optically isotropic character is not due to granule damage but appears to result from lack of selective orientation of the starch chains during granule formation. Badenhuizen *(17)* observed such granules in immature starches from the *ae su* endosperm genotype. On the basis of the discrete x-ray line pattern of the starches, he concluded that the optically isotropic granules were crystalline, not amorphous. Crystallinity has not yet been demonstrated, however, by x-ray patterns of isolated nonbirefringent granules of the Class 5, 6, and 7 starches.

Some spherical granules of the amylomaize starches stain with iodine much more readily than others. This difference in staining can be seen in Figures 2b and 2d of the Class 5 and 7 starches. There appears to be no relation, however, between iodine staining and birefringence; granules stained to the same depth with iodine may or may not show birefringence. The variability in staining indicates differences in surface layers of the granules which affects binding and penetration of iodine; it may possibly result from a variation in amylose distribution among the granules.

When the iodine-staining characteristics of starch granules from ordinary corn are compared with those of starches from amylomaize,

the coloration appears similar if the microscopic examination is made in bright field illumination. However, when iodine-stained granules are examined between crossed polarizers, amylomaize starches with an amylose content above about 65% appear red as against blue for ordinary starch granules (*18*). At relatively low and at intermediate amylose levels, amylomaize starches show a variegated red and blue coloration pattern.

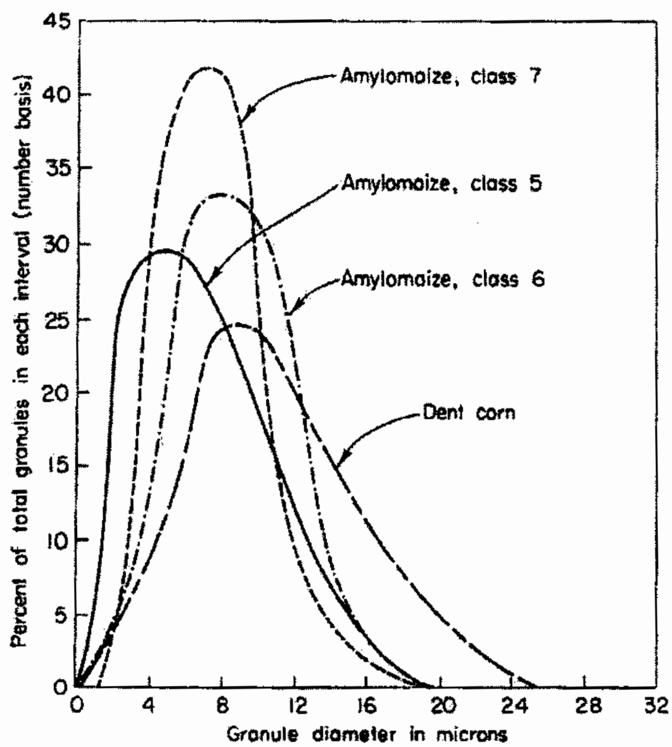

FIG. 3.—Granule size-frequency distribution, number per 2.8 μ interval, for amylomaize starches and ordinary dent corn starch. Identification of starches is as follows: Amylomaize, Class 5, 1963 crop, 62.1% amylose; amylomaize, Class 6, 1959 crop, 66.7% amylose; amylomaize, Class 7, 1962 crop, 72.1% amylose; ordinary dent corn, U.S. 13 hybrid.

The elongated or filamentous granules generally are optically isotropic and show no polarization cross between crossed Nicols. In many cases, however, a low birefringence is evident along the margins of these granules, which indicates molecular orientation in their outermost layers (*16*). The filamentous granules stain less readily with iodine than do the majority of the spherical forms. Frequently the knobs or thickened portions of the filaments are heavily stained while the filamentous portions of the same granule are unstained or only lightly

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stained. The thickened portions often show the typical polarization cross, indicating normal molecular orientation, whereas the rest of the granule remains isotropic.

2. Starch Granule Size Distributions

Size-frequency distributions for amylomaize starches and a dent corn starch are presented in Figures 3 and 4. The distributions are based on microscopic measurements of a large number of granules (*16*). In preparing the mounts for examination, care was taken to avoid orien-

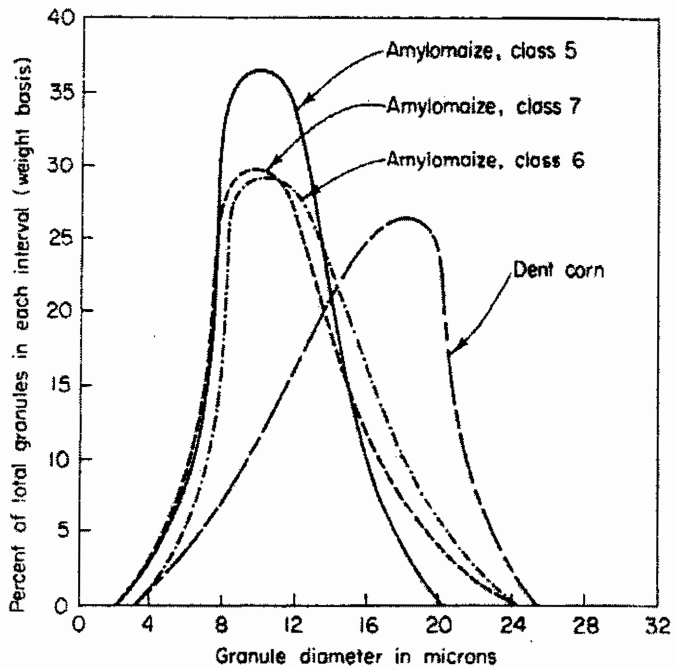

FIG. 4.—Granule size distribution curves, weight per 2.8 μ interval, for amylomaize starches and ordinary dent corn starch. Identification of starches is the same as Figure 3.

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tation of the elongated granules; measurements were made as the field was traversed in a single direction, and the diameter of a granule was taken as the width it presented in the direction of traverse. Distribution curves can be expected to depend on the degree of recovery of starch in processing the grain. Usually a part of the small granule fraction is lost in processing, so that size measurements on the recovered starches are generally higher than the true value. The starches described in Figures 3 and 4 were samples either processed commercially or by methods expected to give recoveries similar to commercial practice. Figure 3 shows that the amylomaize starches contain more small granules than does ordinary corn starch, a difference which is also evident from the

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displacement of the amylomaize starch curves to the left relative to dent corn. The size distributions are narrower for the amylomaize starches than for ordinary starch; the narrower distribution is most evident for the Class 7 starch. Number-average diameters calculated from the curves in Figure 3 are given in Table V. The greater number of large starch granules in ordinary corn starch results in a higher average diameter for this starch.

For some purposes the distribution of weight of starch, rather than the number of granules, according to granule diameter is most important. Weight distribution curves are presented in Figure 4 for the starches given in Figure 3. These curves emphasize the difference between amylomaize starches, as a class, and ordinary corn starch in terms of granule size. As expected, the peaks of the weight distributions are shifted to higher diameters, and since the distributions in Figure 3 have different shapes, the magnitude of the shifts are not the same. Weight-average diameters calculated from the curves in Figure 4 are given in Table V; average diameters are larger, but rank according to diameter is the same as on the number-average basis. For ordinary dent corn starch, Schoch and Maywald (*19*) report a slightly different size distribution for a commercial sample. The respective number- and weight-average diameters for this sample were 9.2 and 14.1 microns.

3. X-Ray Diffraction Patterns

In contrast to ordinary corn starch, which gives an A-type x-ray pattern, amylomaize starches (*20*) give the B-type pattern characteristic of potato starch. Dvonch and co-workers (*21*) first reported the B-pattern for high-amylose starches from su_2, su_2du, and $su^{am}du$ genotypes. Badenhuizen (*17*) later reported that the *ae* and *ae su* endosperms deposited starch with the B-structure. Zobel and co-workers (*20*) concluded from the examination of many different genotypes that the B-structure was obtained only when the *ae* gene was present, regardless of whether the amylose level was above or below that of ordinary starch. The difference from the observations by Dvonch and co-workers (*21*) probably reflects a difference in treatment of the starch samples. In connection with the controlling effect of the *ae* gene on the B-pattern, Sandstedt and co-workers (*22*) found that high-amylose starches with the *ae* gene in their genetic composition were resistant to digestion by pancreatic amylase, as is potato starch, whereas high-amylose starches from other genotypes were more readily digestible. However, differences other than crystal structure are likely involved since sago and arrowroot starches, which give a C-type pattern, are also resistant to pancreatic digestion.

Zobel and co-workers (*20*) also found that the strongest diffraction lines of the V-, or helical, structure appear on x-ray patterns of starches that contained more than about 40% amylose. Their report presents the first x-ray evidence for the helical structure in a native starch; the avid iodine binding and blue staining of starches of normal amylose content suggests, however, that helical or near-helical chain segments are present in ordinary starches. The V-structure in the high-amylose starches appears to be stabilized by the presence of lipid material; the V-pattern is retained after fat extraction but disappears on subsequent slurrying with water. Analyses (*20*) of the amylomaize starches, either by solvent extraction or by hydrolysis, show no significant difference in fat content from that reported for ordinary corn starch.

4. Gelatinization of Amylomaize Starches

Starches with amylose contents in the 20 to 30% range lose their birefringence within a fairly narrow temperature range when heated in water (*19*). A similar phenomenon occurs with high-amylose starches; they differ, however, from starches of ordinary amylose content in that loss of birefringence is not associated with marked granule swelling and development of viscosity at relativity low starch concentrations. Consequently, the temperature at which loss of birefringence occurs for amylomaize starch does not have the same practical significance that it has for ordinary starches; nevertheless, it helps to characterize an amylomaize starch and has been used to aid in distinguishing high-amylose starches from different endosperm genotypes (*23*, *24*). Although Classes 5, 6, and 7 amylomaize starches differ from ordinary corn starch in the temperature at which they lose birefringence, they do not differ significantly among themselves. In the tabulation below, the temperature range over which birefringence loss occurs is defined by three temperatures which correspond to loss of birefringence in the following percentages of granules: first detectable, 50%, and 90%.

Amylomaize starches	66°–68°,	74°–76°,	88°–92°
Ordinary corn starch	61°–62°,	67°–68°,	72°–74°
Maine potato starch	62°–63°,	65°–67°,	72°–73°

In amylomaize starches the crystalline structure responsible for birefringence is more resistant to destruction in hot water than is the crystallinity of ordinary starch. Moreover, the amylomaize starch granules vary more widely in their resistance to destruction; the first 50% of the granules lose birefringence over approximately the same temperature interval as ordinary starch, but destruction of birefringence of the

next 49% of the amylomaize granules requires a 15° temperature interval as compared to a 6° interval for ordinary starch.

Since amylomaize starches have the B-crystal structure, their birefringence-loss range might more properly be compared with that for potato starch, which also has the B-structure. The range for the latter is, however, no higher than that for ordinary corn starch; therefore, crystal structure in itself does not account for the higher temperatures required for the amylomaize starches. Neither does percentage crystallinity since x-ray measurements show that the amylomaize starches are less crystalline than ordinary corn starch (*25*). The high gelatinization temperatures of amylomaize starches cannot be attributed to association through substantially stronger hydrogen bonds; no difference in accessibility of hydroxyl groups to water was found by Taylor and co-workers (*26*) in studies of deuterium exchange. Association of amylose with lipid material also does not account for the high gelatinization temperatures; defatted and nondefatted amylomaize starches show the same gelatinization temperature range.

A possible explanation for the higher temperatures required to initiate gelatinization in amylomaize starches is that more amylose molecules are involved in the crystalline regions of the high-amylose starches than in ordinary starches. The resulting crystallites would have less irregularity of structure due to branch points; such irregularities probably contribute to instability of the crystallites in waxy (100% amylopectin) and ordinary starches. Following this reasoning, an upper limit to the gelatinization temperature range should be observed when a significant fraction of the crystallites are formed only from amylose. Apparently such a limit may have been reached at 88°–92° by the amylomaize starches; this limit needs to be confirmed, however, by observations on crystalline amylose.

Although amylomaize starches do not swell sufficiently in water to give a measurable viscosity in the conventional heating cycle employed in measuring starch pasting properties either in a CIRF viscometer or a Brabender amylograph, the amylomaize starches will gelatinize below 95° by addition of swelling agents such as calcium chloride. Amylograph curves for amylomaize starches in concentrated calcium chloride (sp. gr. 1.30 at 20°) are given in Figure 5.

The amylograph curves of Classes 5, 6, and 7 amylomaize starches are similar except for the maximum viscosity attained. The peak viscosity is greatest for the Class 5 starch and progressively less for Class 6 and Class 7 starches. Marked granule swelling in Class 5 starch, as evidenced by the sharp rise in viscosity, begins at a temperature (41.5°) slightly lower than for the other two classes (about 44°). All starches

reached their peak viscosity at about the same temperature (53.5°–55°); apparently the principal difference between the starches is the capacity of the granules to swell before disintegration and solubilization. Since the capacity for expansion before rupture and distintegration decreases with decreasing amylopectin content, this component appears to contribute importantly to the extensibility of the coherent structure of the swollen granule.

Evidence that amylopectin provides the structural network in gelatinized starch is provided by the observation that most of the amylose

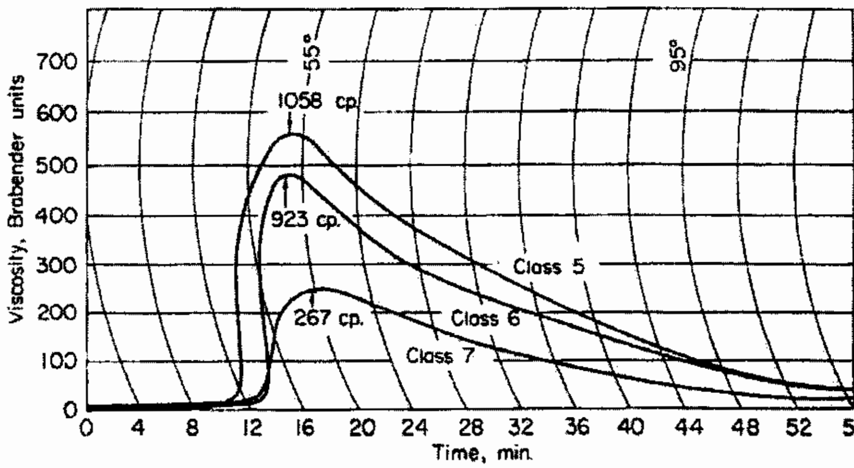

FIG. 5.—Brabender amylograph curves for amylomaize starches in concentrated $CaCl_2$ solution (sp. gr., 1.30 at 20°). Starch concentration, 5 g. (m.f.b.)/100 ml.; heating rate, 1.5°/min.; spindle speed, 75 rpm. Amylomaize, Class 5, 61.8% amylose; amylomaize, Class 6, 66.7% amylose; amylomaize, Class 7, 73.3% amylose.

can be selectively leached from swollen high-amylose starches leaving a gelatinous, coherent residue mainly of amylopectin (*27*). The swelling limit for a starch would be expected, therefore, to depend to a considerable extent on the amount, molecular size, and structure of its amylopectin and the manner in which these molecules are associated into a three-dimensional network.

5. Dispersion of Amylomaize Starches

The term dispersion, as applied here to starch, covers a rather wide range of types of solution. In general, the dissolution of starches involves the successive and overlapping stages of granule swelling, disintegration of the swollen granule, possibly preceded by some leaching out of molecular material, and disaggregation of particles or fragments to a molecular state. When a starch dispersion is prepared by cooking in

water, for example, various proportions of the granules may be at each stage, depending on the conditions and the characteritsics of the starch. For many industrial uses, dispersion largely to the disintegrated granule stage apparently is sufficient. Thus ordinary corn starch finds many applications as a paste prepared by cooking for 30 min. at 90°–95° with moderate stirring. From such a paste, 60–70% may be removed by a 15-min. centrifugation at 2500 rpm. For research on the molecular properties of starch, of course, solution at the molecular level is necessary.

A discussion of the dispersibility of amylomaize starches is complicated by the fact that, in many cases, no critical tests have been applied to determine quantitatively the state of the starch in the dispersion. However, indications of conditions required for dispersion of amylomaize starches are provided by data which have been reported. Some of the apparent inconsistencies probably arise from differences in criteria of dispersions; others may result from differences in the starches.

Amylomaize starches disperse with greater difficulty than does ordinary corn starch, and dispersibility appears to be affected by amylose content and, possibly, by genetic background. Autoclaving at temperatures of 150°–160° generally is required to disperse amylomaize starches sufficiently to withstand centrifugation at $2000 \times G$ for 15 min. with removal of no more than 1 to 2% of starch. Sloan and co-workers (*28*), however, reported that an early Class 5 amylomaize starch, having an amylose content of 50%, was incompletely dispersed at 160°–170° as judged by the presence of intact swollen granules in films prepared from the mixture. These workers found that a mild alkali prewash of the starch with sodium bicarbonate facilitated dispersion, which was then complete at 160°–165° in 1 to 5 min.

By contrast, Anderson and co-workers (*29–31*) dispersed Class 5, 6, and 7 amylomaize starches for fractionation studies in a continuous tube cooker operating at 135°–150° with a retention time of 10 min. Their dispersion was probably aided by subsequent heating at 90° after addition of complexing agent. In still other fractionation studies, a liquid ammonia pretreatment of amylomaize starch was used to loosen the granule structure and permit dispersion at 120° in water or 1-butanol-saturated water (*32, 33*).

Wurzburg and co-workers (*34*) dispersed amylomaize starches by heating in water at 60°–100° after the dry starches were subjected to attrition grinding. The dispersed amylomaize produced firmer gels, and films cast from the dispersed starch were clearer and more continuous than when untreated amylomaize starch was used.

Amylomaize starches can be dispersed in 5–10% concentration at room temperature in 0.5N sodium hydroxide solution. However, in 0.25N

sodium hydroxide, the starches do not disperse but swell to form viscous solutions at 5% concentration. Interestingly, Class 6 starch gives the greatest viscosity rather than one intermediate between the values for Classes 5 and 7, as might be expected on basis of amylose content, and probably demonstrates the effect of genetic background on granule properties (*35*). For potassium hydroxide solutions, Wolff and co-workers (*32*) reported that amylomaize starch, 50% amylose content, was incompletely dissolved at an alkali normality of 0.1–0.2 but was dispersed at normalities of 0.3–1.0.

Amylomaize starches can be dissolved at 10 to 15% concentration in formamide or monoethanolamine by heating at 150° (*28*). Dimethylsulfoxide dissolves high-amylose starch at room temperature (*35–37*). Dispersion is slow, however; and even after 3–4 days of shaking, 2–4% of the amylomaize starches may be removed by centrifugation at $2000 \times G$ (*35*). Aqueous dimethylsulfoxide (80–95%) dissolves starch more rapidly than the anhydrous solvent; centrifugation at $2000 \times G$ after 24-hr. shaking removes only a trace of undissolved material (*36*).

Amylomaize starch (Class 7) pretreated by dispersion in dimethylsulfoxide and quantitatively precipitated with alcohol has increased water solubility. The pretreated starch showed a V x-ray diffraction pattern (*38*).

In terms of molecular dispersion, the best solvent for amylomaize starch at room temperature, according to Erlander and co-workers (*39*), is a concentrated aqueous solution containing lithium thiocyanate (5*M*) and guanidinium thiocyanate (2*M*). After 24 hr. in this solvent, only a trace of residue was removed by centrifugation at $39{,}000 \times G$. In 90% aqueous dimethylsulfoxide, however, molecular dispersion was not reached after 24 hr. shaking for a Class 7 amylomaize starch (*39*); centrifugation at 18,000 rpm. ($39{,}000 \times G$) for 15 min. removed 11% of the starch. These workers also found that aggregates sufficiently large to be removed by 15-min. centrifugation at $39{,}000 \times G$ were present in *N* potassium hydroxide dispersions. Even after 24-hr. shaking, 12% of the starch was precipitated from the dispersion by centrifugation.

6. Molecular Components of Amylomaize Starches

Iodine affinities, intrinsic viscosities, and β-amylase conversion data are given in Table VI for amylose fractions from several high-amylose starches (*40*) and from ordinary corn starch. These data were obtained from fractions isolated from starches subjected to a neutral chemical steep (*41*). In comparison with the intrinsic viscosity in *N* potassium hydroxide of 1.7 in Table VI, amylose fractions isolated by conventional laboratory wet-milling procedures showed intrinsic viscosities of 1.4 in

the same solvent (*27*), which indicates a somewhat lower molecular size for the amylose. Molecular weight of two amylose samples with the lower viscosity were 283,000 and 334,000 in comparison with 312,000 for ordinary corn amylose as determined by light scattering (*27*). The data from these investigations, together with the periodate oxidation and β-amylase conversion data of Wolff and co-workers (*32*), show that

Table VI

Amylose Fractions from High-Amylose Corn Starches

Starch		*Amylose*					
Source	*Apparent amylose* (%)	[η] *N KOH*	*Iodine affinity* (*mg. I_2/g.*)	*β-Amylase conversion* (*% maltose*)	*Average length of unit chain*	*Length of inner branch*	*Length of outer branch*
Hybrid	59	1.68–1.73	206	96	502	16	486
Hybrid	67	1.68–1.72	205	96	502	16	486
Inbred	68	1.63–1.67	206	98	509	17	496
Hybrid	71	1.63–1.68	206	—	—	—	—
Hybrid[a]	27	1.78	204	96	503	16	497

[a] Ordinary corn.

the amylose component of the high-amylose starches is like that of ordinary corn starch in molecular structure and size.

The amylopectin component of high-amylose starches differs both in structure and molecular size from the branched component of ordinary

Table VII

Properties of Amylopectins of High-Amylose Corn Starch

Starch		*Amylopectin*						
Source	*Apparent amylose* (%)	[η] *N KOH*	*Iodine affinity* (*mg. I_2/g.*)	*Amylose equivalent* (%)	*β-Amylase conversion* (*% maltose*)	*Average length of unit chain*	*Length of inner branch*	*Length of outer branch*
Hybrid	50	1.2	51	—	58	—	—	—
Inbred	50	1.2	53	26	62	36	11.7	24.3
Hybrid	57	1.2	79	40	66	40	11.3	28.7
Hybrid	67	1.2	83	41	73	42	10	32
Inbred	68	1.2	85	43	74	43	10	33
Hybrid	71	1.2	89	45	77	45	10	35
Hybrid[a]	27	1.8	12	5	56	27	10	17

[a] Isolated from ordinary corn; steeped in water at 37°C.

corn starch. Periodate oxidation data (*32*) show that the average chain length of the first amylopectin listed in Table VII is 36 D-glucose units as compared with 27 units for ordinary starch amylopectin, but these data do not differentiate between lengths of inner and outer chains of the branched molecule. Evidence that increased length of outer branches accounts for part, if not all, of the increase in average chain length is provided by both the greater iodine affinity, as measured by potentiometric titration, and the higher β-amylase conversion limit for the amylopectins of the high-amylose starches listed in Table VII (*40*). Moreover, the differences between amylopectins are magnified as the amylose content of the starch is increased (*40*).

The tendency of high-amylose starch amylopectins to retrograde from solution at 25° (*27*), resembling amylose in this respect, is further evidence for an increased chain length of outer branches and a more linear structure. The retrograded amylopectins differ from retrograded amylose, however, in that they can be at least partially dissolved on heating at 98°; retrograded amylose requires autoclaving for dissolution. The possibility that retention of amylose in the amylopectin might account for observed differences has been eliminated by ultracentrifugation studies (*27*). No fraction having a sedimentation rate comparable to amylose or smaller molecules was observed in alkaline solutions of these amylopectin preparations.

On the basis of intrinsic viscosities (Table VII), the molecular weight of high-amylose starch amylopectin is less than that of ordinary corn starch amylopectin. This difference is confirmed by molecular weight determinations by light scattering (*39*), which gives values of 9.6 million for amylopectin from a high-amylose starch containing 71% apparent amylose as compared to 1.5 billion for amylopectin isolated from ordinary starch by the same procedure and examined in the same solvent system.

7. Chemically Modified Amylomaize Starch

Swelling and dispersibility of amylomaize starches in hot water, as well as stability of their solutions toward gel formation or retrogradation, are greatly increased by relatively low degrees of chemical derivatization. Rankin and co-workers (*42*) prepared hydroxyethyl ether derivatives of amylomaize starch (50% apparent amylose content) containing from 1% to 27% by weight combined ethylene oxide. At ethylene oxide contents of 5% to 7%, corresponding to 0.17 to 0.24 of hydroxyethyl groups per D-glucose unit, the modified starches on heating at 90° form viscous pastes that remain fluid on cooling to room temperature, even after standing several days. The relatively low light trans-

mittancy (29% at 650 mμ for 1% concentration) of the pastes indicates incomplete dispersion; this was confirmed by microscopic examination which showed that about 20% of the granules at degree of substitution (D.S.) 0.24 remained in suspension, swollen but undisintegrated. Despite the greater clarity of its paste (69%), ordinary corn starch at the same D.S. and temperature does not completely disperse but 15% of the granules remain in suspension. These granules, swollen much more than the amylomaize granules, are responsible for the greater viscosity and clarity of the ordinary starch pastes.

Rankin and co-workers (*42*) also found that hydroxyethylated amylomaize starches dispersed at 90° form films superior to those of ordinary or waxy corn starch of the same D.S. The relatively low strength properties they report very likely reflect incomplete dispersion in the solutions from which the films were cast and the consequent inhomogeneities in the films. Roth and Mehltretter (*43*) report that films from hydroxypropylated amylomaize starch of 71% apparent amylose has reduced tensile strength but increased elongation and burst strength when compared to film from the original starch.

Hypochlorite oxidation of amylomaize starch increases dispersibility on the introduction of fewer new functional groups than are required in hydroxyethylation (*44*). A 6% level of oxidation, or 6 moles of carboxyl and carbonyl groups per 100 D-glucose units (essentially comparable to D.S. = 0.06), is required to obtain a product from amylomaize starch (50% apparent amylose) that yields a relatively stable paste. At 9.8% oxidation level, this high-amylose starch gives very clear, nonsettling pastes that exhibit no setback. Oxidized amylomaize starch granules swell less on heating to 90° than ordinary corn starch granules do at comparable levels of oxidation; 8% to 14% starch concentrations are required to give viscosities comparable to 5% concentrations of oxidized ordinary corn starch.

Sloan and co-workers (*45*) prepared the carboxymethyl derivative of amylomaize starch, 57% amylose content, by a method that avoids dissolving the granule (*46*). At D.S. 0.05, the carboxymethylstarch is not soluble in boiling water; products of D.S. 0.1 disperse at 50°–60°, whereas above D.S. 0.2 the products are cold water soluble. Viscosity properties are typical of a polyelectrolyte and the addition of salt markedly reduces viscosity. Compared to similar derivatives of ordinary starch and cellulose, the carboxymethyl amylomaize starches give less viscous solutions, but the viscosity is stable over the heating and cooling range of the pasting procedure in both neutral and alkaline solutions. Soil-suspending activity of carboxymethyl amylomaize starch (*45*) is superior to that of ordinary starch derivatives. At D.S. 0.7, maximum

activity is reached and is about two-thirds that of a commercial carboxymethylcellulose.

Other derivatives of amylomaize starches are reported to impart solubility at low degrees of substitution (*37*). These include the maleate, sulfate, formate, benzoate, and acetate esters, and the methyl, ethyl, allyl, hydroxyethyl, benzyl, and cyanoethyl ethers.

V. Uses for Amylomaize Starches

At the outset of the high-amylose starch program, it was thought that an amylose content of 80–85% would need to be attained before the new starch could find industrial use. This prediction was based largely on the assumption that high-amylose starch would be used as a film-forming material, and it had been demonstrated earlier by Wolff and co-workers (*47*) that 80–85% of corn amylose in mixture with corn amylopectin was required to give mechanical properties approaching those for pure amylose in unsupported films. Class 5 amylomaize starches, however, found application soon after the development of agronomically suitable hybrids. An early use was as a sizing material for glass fibers (*48*); this is applied at the spinnerets to protect the fibers from breakage resulting from fiber-to-fiber abrasion and also to improve fiber handling on the bobbins. A particular advantage of the amylomaize starches is the rapid development of strength in the coating; this is sufficient to resist the centrifugal forces (about $3000 \times G$) encountered during high-speed winding of the fiber tow on spools and to retard migration of the size under the internal pressure to which the fibers are subjected on the spools.

Other applications of amylomaize starches will also depend on the properties of their films as deposited on various substrates where they may serve either as a coating to improve surface properties or as an adhesive to bind particles together. Experimentation with these starches is underway in many industries, but information on usage is not available. The properties of the new starches suggest that applications may be found in the manufacture of paper and paper products.

Pearl (*49*) has shown that amylose is adsorbed from aqeuous solution by wood pulp at a greater rate and in greater amount than amylopectin at comparable concentration. Others had earlier reported that amylose is selectively adsorbed from starch solutions by cellulose fibers (*50, 51*). The binding of amylose by cellulose appears to be largely irreversible (*49, 50*) whereas amylopectin can be completely eluted with hot water. This stronger binding of amylose to cellulosic fibers should give superior properties to amylomaize starches as beater additives or surface sizes. Indeed, laboratory experiments with unmodified Class 5

amylomaize starch have shown it to be an effective beater adhesive if it is well dispersed before addition to the pulp furnish (*52*). The unmodified starch also gave favorable results when evaluated as a surface size. Sizes prepared by solution in alkali provide excellent strength properties; however, strongly alkaline sizes are not recommended since the alkali tends to increase the rate of water absorption by the paper. Other means of stabilization of the amylomaize starch at the concentrations required in sizing must be used; either the bath needs to be maintained above 60°–70° to prevent retrogradation of the amylose, or the starch should be chemically modified as discussed in the preceding section.

The possible utility of amylomaize starches as self-supporting films has received attention. The mechanical properties of films cast from unfractionated Class 5 and Class 7 amylomaize starches (*53*) were comparable to those reported for films of similar composition made from synthetic mixtures of amylose and amylopectin (*47*). The very low permeability of amylose films to oxygen (*54, 55*) is also a characteristic of amylomaize starch films. This property suggests their use as an oxygen barrier, either as a wrapping or a coating.

A pilot plant capable of producing over 800,000 pounds of film annually from amylomaize starch, dedicated in 1965 by a commercial corn wet miller, has brought closer to reality the dream of corn breeders and starch chemists that amylomaize would become an industrial commodity (*56, 57*).

Amylomaize is a new crop now beyond the early stages of its development. New hybrids will continue to be bred with improved agronomic characteristics and yielding starches with even higher amylose contents. Changes in composition of the kernel, including increase of starch content, also may prove possible. Attainment of the original goal of 80–85% amylose content in the starch appears certain, and ultimately higher levels may be realized at least as "apparent" amylose. Undoubtedly, many uses that require the properties of linear starch molecules, in varying degree, will be served by one or another of the amylomaize starches now avialable or under development.

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